Supporting Information

For

N-Heterocyclic Olefin Stabilized Boron Dication

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General Information:

All experimental procedures are carried under N_2 atmosphere using standard Schlenk techniques or inside a glove box. Hexane was degased and dried with molecular sieves packed column under nitrogen. Chlorobenzene, 1,2-difluorobenzene, diethyl ether, C_6D_6, CD_2Cl_2 and CD_3NO_2 were dried with appropriate drying agents and distilled under nitrogen atmosphere (CaH_2 for chlorobenzene, 1,2-difluorobenzene and CD_3NO_2; P_2O_5 for CD_2Cl_2; Na/K alloy for ether and C_6D_6). 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene olefin (NHO) was prepared according to the published procedures.[1] ^1H, ^{11}B, ^{13}C and ^{31}P NMR spectra were recorded using Bruker AVIII 400 MHz NMR spectrometer. Chemical shifts are reported in ppm (δ) with respect to the signal of solvent residual (^1H and ^{13}C NMR) or external standards (BF_3-OEt_2 for ^{11}B NMR and phosphoric acid for ^{31}P NMR). Elemental analysis was performed on a Heraeus varioIII-NCH elemental analyzer.

Synthesis:

Cp*BCl_2-NHO adduct (1): A solution of NHO (200 mg, 0.50 mmol) in hexane (5 mL) was allowed to react with Cp*BCl_2 (108 mg, 0.50 mmol) at room temperature for 3 hours. White powder was insoluble in hexane, and was collected by filtration to yield **1** (280 mg, yield: 90 %). ^1H NMR (C_6D_6, 400.2 MHz, ppm): δ 7.21 (t, 2 H, *p*-Dipp), 7.06 (d, 4 H, *m*-Dipp), 6.42 (s, 2 H, NCH), 2.65~2.72 (m, 4 H, C*H*Me_2), 1.99 (s, 2H, IPr=C*H_2*), 1.96 (s, 6H, Cp*), 1.71 (s, 6H, Cp*), 1.63 (s, 3H, Cp*), 1.39 (d, 12 H, CH*Me_2*), 0.90 (d, 12 H, CH*Me_2*); ^{11}B NMR (128.4 MHz, C_6D_6, ppm): δ = 7 ppm; ^{13}C NMR (C_6D_6, 100.6 MHz, ppm): δ 160.3 (NCN), 146.0 (Cp*), 145.8 (*ipso*-C, Dipp), 132.2 (*o*-C, Dipp), 131.6 (Cp*), 131.3 (*p*-C, Dipp), 124.9 (*m*-C, Dipp), 122.0 (NCH), 58.5 (Cp*), 29.3 (*C*HMe_2, Dipp), 26.4 (CH*Me_2*, Dipp), 25.1 (CH_2), 22.3 (CH*Me_2*, Dipp), 17.1 (Me, Cp*), 14.7 (Me, Cp*), 11.5 (Me, Cp*). Anal. Calcd. for $C_{38}H_{53}N_2BCl_2$: C, 73.67; H, 8.62; N, 4.52. Found: C, 72.88; H, 8.42; N, 4.57.

[Cp*BCl-NHO][OTf] ([2][OTf]): Compound **1** (51 mg, 0.08 mmol) and excess TMSOTf (48 mg, 0.22 mmol) were mixed in 2 mL of benzene in a vial inside a glove box. The reaction mixture was allowed to sit at room temperature for 24 hours to yield colorless crystalline products. After filtration and dried under vacuum, [**2**][OTf] was isolated as white solid (41 mg, yield: 67.9 %). Single crystals of [**2**][OTf] and [**2**][$AlCl_4$] were obtained from solution consisting of **1** (15 mg, 0.02 mmol) and one equivalent of TMSOTf or $AlCl_3$ in C_6D_6 (0.4 mL). ^1H NMR (CD_2Cl_2, 400.2 MHz, ppm): δ 7.71 (s, 2 H, NCH), 7.70 (t, 2 H, *p*-Dipp), 7.47 (d, 4 H, *m*-Dipp), 2.34~2.44 (m, 4 H, C*H*Me_2), 2.26 (s, 2H, IPr=CH_2), 1.38 (s, 15H, Cp*),

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[1] Y. Wang, M. Y. Abraham, R. J. Gilliard, D. R. Sexton, P. Wei and G. H. Robinson, *Organometallics*, 2013, **32**, 6639-6642.

1.31 (d, 12 H, CH*Me*$_2$), 1.23 (d, 12 H, CH*Me*$_2$); ^{11}B NMR (128.4 MHz, CD_2Cl_2, ppm): δ = 66 ppm; ^{13}C NMR (CD_2Cl_2, 100.6 MHz, ppm): δ 150.2 (NCN), 145.6 (*o*-C, Dipp), 133.2 (*p*-C, Dipp), 129.5 (*ipso*-C, Dipp), 129.0 (NCH), 126.3 (*m*-C, Dipp), 125.6 (C_5, Cp*), 125.5 (C_5, Cp*), 29.8 (*C*HMe_2, Dipp), 26.5 (CH*Me*$_2$, Dipp), 23.0 (CH*Me*$_2$, Dipp), 20.7 (CH_2), 12.2 (Me-C5, Cp*). Anal. Calcd. for $C_{39}H_{53}N_2BClSO_3F_3$: C, 63.89; H, 7.29; N, 3.82. Found: C, 62.95; H, 7.06; N, 3.77.

[Cp*B-NHO][AlCl$_4$]$_2$ ([3][AlCl$_4$]$_2$): Compound **1** (105 mg, 0.17 mmol) and excess $AlCl_3$ (100 mg, 0.75 mmol) were mixed in 5 mL of chlorobenzene in a glove box to yield amber oil at the bottom of the reaction flask. After stirring for additional two hours at 80 ^{o}C, ether (15 mL) was added to the reaction mixture to convert the amber oil into pale pink solid. The solid was then collected and washed with ether for three times to yield [**3**][$AlCl_4$]$_2$ (128 mg, yield: 85 %). Single crystals of [**3**][$AlCl_4$]$_2$ were obtained from slow cooling a saturated difluorobenzene solution of [**3**][$AlCl_4$]$_2$ from 80 ^{o}C to room temperature inside a glove box. To replace [$AlCl_4$]$^-$, large excess of TMSOTf (0.1 mL) was added to a [**3**][$AlCl_4$]$_2$ suspension in difluorobenzene (128 mg, 0.14 mmol). The resulting mixture was allowed to stir at room temperature for 4 hours before the addition of ether (15 mL). The resulting white solids were collected and washed with ether for three times to give [**3**][OTf]$_2$ (108 mg, yield: 89 %). Since [**3**][$AlCl_4$]$_2$ is not stable in solution, only the spectral data of [**3**][OTf]$_2$ are reported. ^{1}H NMR (CD_3NO_2, 400.2 MHz, ppm): δ 8.00 (s, 2 H, NCH), 7.84 (t, 2 H, *p*-Dipp), 7.69 (d, 4 H, *m*-Dipp), 2.35~2.42 (m, 4 H, C*H*Me_2), 2.16 (broad, 2H, IPr=CH_2), 1.89 (s, 15H, Cp*), 1.47 (d, 12 H, CH*Me*$_2$), 1.21 (d, 12 H, CH*Me*$_2$); ^{11}B NMR (128.4 MHz, C_6D_6, ppm): δ = - 45.9 ppm; ^{13}C NMR (CD_3NO_2, 100.6 MHz, ppm): δ140.7 (*o*-C, Dipp), 139.0 (NCN), 129.3 (*p*-C, Dipp), 125.1 (*ipso*-C, Dipp), 122.7 (NCH), 122.4 (*m*-C, Dipp), 109.9 (C_5, Cp*), 25.4 (*C*HMe_2, Dipp), 20.8 (CH*Me*$_2$, Dipp), 17.4 (CH*Me*$_2$, Dipp), 6.9 (Me, Cp*), -5.51 (CH_2). Anal. Calcd. for $C_{38}H_{53}N_2BAl_2Cl_8$ ([**3**][$AlCl_4$]$_2$) : C, 51.50; H, 6.03; N, 3.16. Found: C, 51.27; H, 6.01; N, 2.82.

Lewis Acidity Measurements:

The Lewis acidity of $B(C_6F_5)_3$, [**3**]$^{2+}$ and [**D**]$^{2+}$ was determined with the Gutmann-Beckett method using the ^{31}P NMR chemical shift change of Et_3PO in CD_3NO_2. In all cases, Lewis acids were mixed with one equivalent of Et_3PO in CD_3NO_2, and the measured ^{31}P NMR resonances were compared to the value determined for free Et_3PO in CD_3NO_2 (50.5 ppm). The ^{31}P NMR signals at 79.8, 80.1, and 52.4 ppm were observed for $B(C_6F_5)_3$, [**3**]$^{2+}$ and [**D**]$^{2+}$, respectively.

X-ray Crystallography:

Diffraction data of **1**, [**2**][OTf], [**2**][$AlCl_4$], and [**3**][$AlCl_4$]$_2$ were collected at T = 200(2) K with a Bruker AXS APEX CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. Cell parameters were retrieved and refined using DENZO-SMN software on all reflections. Data reduction was performed with DENZO-SMN software. Structural analysis was conducted with SHELXTL, and the structure was solved and refined using SHELXL-97 by full-matrix least-squares on F^2 values. Hydrogen atoms were added to the structure models in calculated positions. Crystallographic data of **1**, [**2**][$AlCl_4$], [**2**][OTf], and [**3**][$AlCl_4$]$_2$ have been deposited at the Cambridge Crystallographic Data Center with deposition number of CCDC-1429029, CCDC-1429031, CCDC-1429030, and CCDC-1429032, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

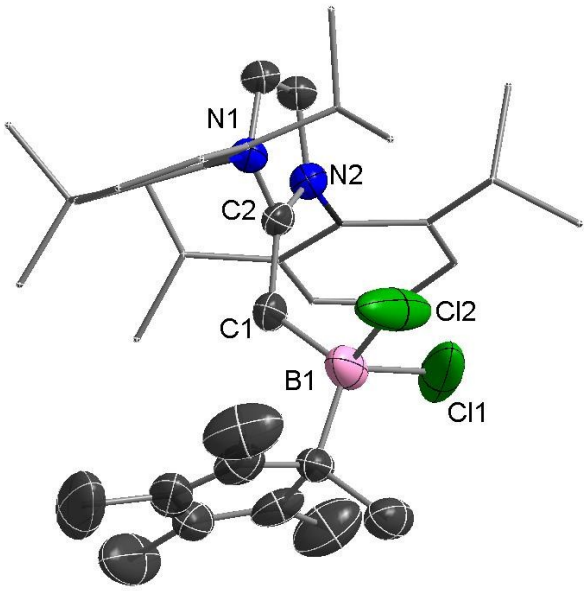

Figure S1: Molecular structure of **1**.

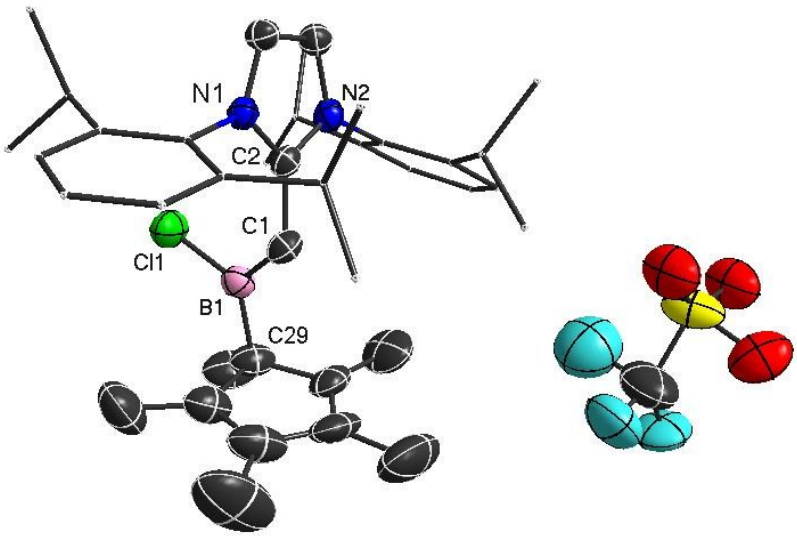

Figure S2: Molecular structure of [**2**][OTf].

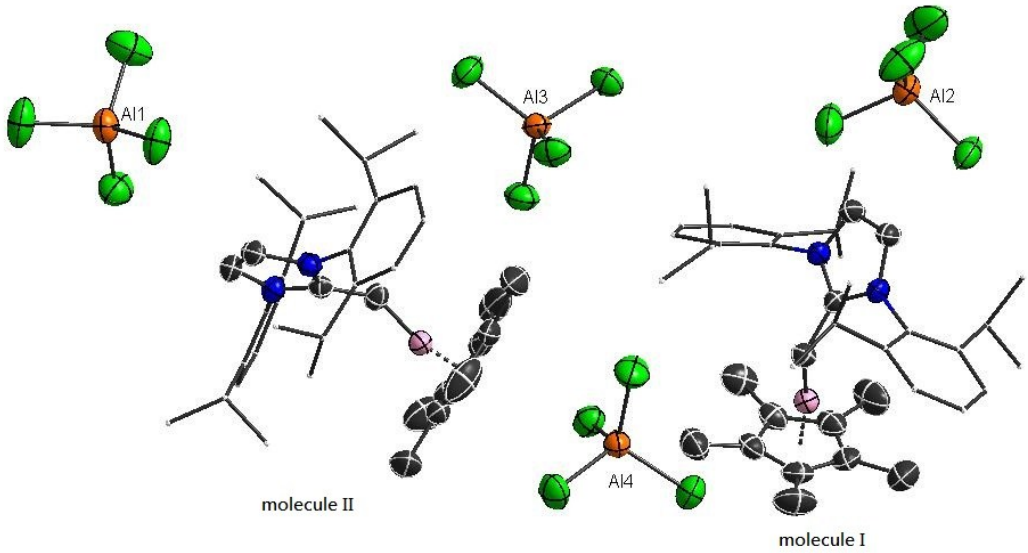

Figure S3: The two independent molecules found in the crystal data of [**3**][$AlCl_4$]$_2$.

Table S1. Crystal data and structure refinement for ic17103. (**1**)

Identification code	ic17103	
Empirical formula	C56 H71 B Cl2 N2	
Formula weight	853.86	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.1478(3) Å	α= 90°.
	b = 16.7606(5) Å	β= 90°.
	c = 30.0835(6) Å	γ = 90°.
Volume	5116.7(2) $Å^3$	
Z	4	
Density (calculated)	1.108 Mg/m_3	
Absorption coefficient	0.163 mm^{-1}	
F(000)	1840	
Crystal size	0.50 x 0.16 x 0.07 mm_3	
Theta range for data collection	1.35 to 25.00°.	
Index ranges	-12<=h<=11, -14<=k<=19, -35<=l<=35	
Reflections collected	17499	
Independent reflections	8793 [R(int) = 0.0523]	
Completeness to theta = 25.00°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9887 and 0.9228	
Refinement method	Full-matrix least-squares on F_2	
Data / restraints / parameters	8793 / 18 / 563	
Goodness-of-fit on F2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0645, wR2 = 0.1542	
R indices (all data)	R1 = 0.1407, wR2 = 0.1827	
Absolute structure parameter	0.00(17)	
Largest diff. peak and hole	0.449 and -0.428 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for ic17094. ([**2**][OTf])

Identification code	ic17094	
Empirical formula	C45 H59 B Cl F3 N2 O3 S	
Formula weight	811.26	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.6683(3) Å	α= 90°.
	b = 11.9885(3) Å	β= 91.8376(12)°.
	c = 32.9526(7) Å	γ = 90°.
Volume	4607.22(19) $Å^3$	
Z	4	
Density (calculated)	1.170 Mg/m^3	
Absorption coefficient	0.179 mm^{-1}	
F(000)	1728	
Crystal size	0.50 x 0.10 x 0.10 mm^3	
Theta range for data collection	1.24 to 25.00°.	
Index ranges	-13<=h<=13, -13<=k<=14, -39<=l<=25	
Reflections collected	16645	
Independent reflections	8079 [R(int) = 0.0557]	
Completeness to theta = 25.00°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9823 and 0.9158	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8079 / 120 / 512	
Goodness-of-fit on F^2	1.140	
Final R indices [I>2sigma(I)]	R1 = 0.1182, wR2 = 0.2762	
R indices (all data)	R1 = 0.2215, wR2 = 0.3293	
Largest diff. peak and hole	1.328 and -1.553 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for ic17095. ([**2**][$AlCl_4$])

Identification code	ic17095	
Empirical formula	C41 H56 Al B Cl5 N2	
Formula weight	791.92	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.9267(6) Å	α= 90°.
	b = 13.7987(5) Å	β= 90.2460(10)°.
	c = 21.4098(8) Å	γ = 90°.
Volume	4409.7(3) $Å^3$	
Z	4	
Density (calculated)	1.193 Mg/m^3	
Absorption coefficient	0.378 mm^{-1}	
F(000)	1676	
Crystal size	0.40 x 0.30 x 0.28 mm^3	
Theta range for data collection	1.36 to 25.00°.	
Index ranges	-17<=h<=16, -16<=k<=16, -25<=l<=25	
Reflections collected	26560	
Independent reflections	7766 [R(int) = 0.0368]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9015 and 0.8634	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7766 / 304 / 490	
Goodness-of-fit on F^2	1.152	
Final R indices [I>2sigma(I)]	R1 = 0.0680, wR2 = 0.1604	
R indices (all data)	R1 = 0.0841, wR2 = 0.1729	
Largest diff. peak and hole	0.731 and -0.423 $e.Å^{-3}$	

Table S4. Crystal data and structure refinement for ic17210. ([**3**][$AlCl_4$]$_2$)

Identification code	ic17210	
Empirical formula	C50 H61 Al2 B Cl8 F4 N2	
Formula weight	1114.38	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.3983(4) Å	α= 71.8270(7)°.
	b = 20.8463(6) Å	β= 86.9293(8)°.
	c = 23.5587(7) Å	γ = 85.3593(7)°.
Volume	5763.7(3) Å^3	
Z	4	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	0.468 mm^{-1}	
F(000)	2312	
Crystal size	0.40 x 0.40 x 0.30 mm^3	
Theta range for data collection	0.91 to 27.50°.	
Index ranges	-16<=h<=16, -27<=k<=27, -30<=l<=30	
Reflections collected	68005	
Independent reflections	26408 [R(int) = 0.0394]	
Completeness to theta = 27.50°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8723 and 0.8348	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	26408 / 162 / 1233	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0822, wR2 = 0.2096	
R indices (all data)	R1 = 0.1327, wR2 = 0.2442	
Largest diff. peak and hole	1.275 and -0.503 e.Å^{-3}	

DFT calculations:

All geometries optimization and energy calculations were performed with the Gaussian 09 program package and B3LYP density functional. The basis set employed for the calculations were 6-311G(d, p) for all atoms. Frequency calculations were performed to verify the optimized structures as minima**.** The solvation effects of nitromethane were evaluated using the polarized continuum model (PCM) with the universal force field (UFF) radii built from the UFF force field. The electron potential surface was generated by GaussView 5.0.8.

Table S5. CIA of $[\mathbf{3}]^{2+}$ and $[\mathbf{D}]^{2+}$

The chloride ion affinity (CIA) was calculated according to the following reactions:	
$[\mathbf{3}]^{2+} + AlCl_4^- \rightarrow [\mathbf{2}]^+ + AlCl_3$	$\Delta H(MeNO_2) = 21.2$ kcal/mol
$[\mathbf{D}]^{2+} + AlCl_4^- \rightarrow [\mathbf{D}{+}Cl]^+ + AlCl_3$	$\Delta H(MeNO_2) = 35.7$ kcal/mol

Table S6. Cartesian coordinate of $\mathbf{[3]^{2+}}$

SCF energy (B3LYP/6-311g**) = -1614.43031587 hartree
Solvation: nitromethane with PCM

Atom	Coordinates (Angstroms) X	Y	Z
B	-0.281431	1.743162	-1.166914
N	-0.963162	-1.114334	1.009301
N	1.207690	-1.056962	0.875490
C	-0.000328	0.193248	-0.960348
H	-0.743412	-0.319685	-1.578725
H	0.957263	0.011249	-1.455327
C	0.069705	-0.565924	0.327378
C	-0.469016	-1.964854	1.984623
H	-1.123049	-2.516447	2.635361
C	0.880125	-1.929003	1.902675
H	1.634522	-2.449096	2.463651
C	-2.384018	-0.944217	0.740889
C	-2.943018	-1.700161	-0.311872

C	-4.301457	-1.520317	-0.582886
H	-4.762601	-2.081523	-1.385778
C	-5.074096	-0.650275	0.174933
H	-6.125238	-0.518503	-0.053441
C	-4.505873	0.032162	1.240668
H	-5.123419	0.685401	1.846625
C	-3.149872	-0.101219	1.569475
C	-2.167098	-2.761712	-1.088242
H	-1.106707	-2.671071	-0.846969
C	-2.304694	-2.615211	-2.614055
H	-3.332328	-2.784345	-2.944353
H	-1.672096	-3.352718	-3.113792
H	-2.002790	-1.623624	-2.960328
C	-2.602863	-4.171574	-0.636598
H	-2.466342	-4.308125	0.438681
H	-2.010313	-4.930241	-1.154364
H	-3.656612	-4.347308	-0.868553
C	-2.711657	0.622811	2.849763
H	-3.352832	1.508586	2.888941
C	-1.268345	1.135264	2.956054
H	-1.213559	1.866041	3.766247
H	-0.937370	1.635119	2.045993
H	-0.557785	0.343685	3.195877
C	-3.068721	-0.225877	4.090098
H	-2.462593	-1.134100	4.142117
H	-4.119901	-0.520654	4.082679
H	-2.882976	0.351531	4.999647
C	2.579342	-0.845326	0.425247
C	3.053050	-1.626494	-0.647208
C	4.381891	-1.433352	-1.037749
H	4.783819	-2.012647	-1.859544
C	5.200600	-0.527785	-0.377321
H	6.228812	-0.398485	-0.694644
C	4.713160	0.201061	0.700541
H	5.372661	0.886675	1.216330
C	3.391919	0.061501	1.135118
C	2.220401	-2.700600	-1.340455
H	1.181867	-2.598862	-1.021092
C	2.238021	-2.569260	-2.874118
H	1.936256	-1.571210	-3.200901
H	1.547411	-3.292798	-3.314122
H	3.230635	-2.770886	-3.283812
C	2.685952	-4.105992	-0.907587
H	3.719666	-4.285312	-1.214710
H	2.056743	-4.869267	-1.372750
H	2.628748	-4.232212	0.176083
C	2.915426	0.821628	2.368937

H	1.825247	0.880288	2.333790
C	3.451649	2.262727	2.435112
H	2.940029	2.809246	3.230875
H	3.301748	2.801716	1.497823
H	4.520167	2.286324	2.662262
C	3.306032	0.071583	3.660930
H	4.393538	-0.007187	3.742792
H	2.894449	-0.938255	3.697857
H	2.938206	0.615698	4.534736
C	-0.140394	3.371527	-0.541829
C	-1.472352	3.014163	-0.962056
C	-1.391707	2.517597	-2.305812
C	-0.020210	2.568075	-2.717564
C	0.754215	3.090587	-1.630497
C	0.257481	3.927410	0.790382
H	0.528680	4.977595	0.656634
H	1.116298	3.409634	1.213256
H	-0.559280	3.884697	1.507061
C	-2.727647	3.122971	-0.155080
H	-2.524831	3.176063	0.912371
H	-3.402185	2.288566	-0.339654
H	-3.240581	4.043924	-0.444845
C	-2.529146	1.943546	-3.091571
H	-3.049599	2.759559	-3.599907
H	-3.248832	1.434447	-2.451347
H	-2.182421	1.243760	-3.850789
C	0.530745	2.051389	-4.010332
H	-0.025958	1.188816	-4.375141
H	1.580655	1.776880	-3.920174
H	0.453520	2.842060	-4.761434
C	2.247317	3.220647	-1.610382
H	2.746613	2.286910	-1.874788
H	2.603387	3.537013	-0.632572
H	2.545598	3.977887	-2.339066

Table S7. Cartesian coordinate of **[2]**$^{+}$

SCF energy (B3LYP/6-311g**) = -2074.87615698 hartree
Solvation: nitromethane with PCM

Atom	Coordinates (Angstroms)		
	X	Y	Z
B	0.313036	1.052542	-1.490313

Cl	-0.130482	-0.048111	-2.819629
N	-1.405443	-1.465470	0.538111
N	0.746161	-1.784255	0.534943
C	-0.013014	0.578188	-0.001268
H	-0.943104	1.100632	0.248302
H	0.740438	0.989652	0.673472
C	-0.216247	-0.858855	0.316302
C	-1.184684	-2.785971	0.906129
H	-1.996200	-3.448701	1.145615
C	0.152349	-2.983861	0.905013
H	0.737976	-3.852645	1.145603
C	-2.725192	-0.849329	0.512933
C	-3.562460	-1.089995	-0.593594
C	-4.834636	-0.510217	-0.565930
H	-5.509422	-0.672014	-1.396923
C	-5.251807	0.264850	0.508475
H	-6.242015	0.705642	0.504079
C	-4.410375	0.464399	1.594996
H	-4.757573	1.052432	2.435417
C	-3.129779	-0.095473	1.632571
C	-3.167148	-1.982942	-1.765010
H	-2.087040	-2.135602	-1.730009
C	-3.841002	-3.366119	-1.647948
H	-3.590817	-3.866774	-0.710012
H	-4.929526	-3.272934	-1.696881
H	-3.519500	-4.010390	-2.470679
C	-3.492024	-1.348755	-3.129365
H	-3.069185	-0.346690	-3.217109
H	-3.073852	-1.964821	-3.929649
H	-4.569628	-1.280949	-3.298460
C	-2.277308	0.074401	2.886597
H	-1.268747	-0.284485	2.675241
C	-2.831166	-0.793726	4.034720
H	-2.880514	-1.847617	3.750804
H	-2.188481	-0.707698	4.914918
H	-3.837341	-0.472555	4.317631
C	-2.148139	1.544423	3.323394
H	-1.463381	1.618306	4.172001
H	-1.758094	2.171557	2.518348
H	-3.108638	1.959364	3.638476
C	2.188262	-1.580247	0.514573
C	2.918319	-2.005327	-0.613083
C	4.305090	-1.829112	-0.574076
H	4.904039	-2.141178	-1.420055
C	4.931983	-1.272448	0.533721
H	6.008542	-1.146684	0.537967
C	4.186592	-0.892273	1.641922

H	4.690990	-0.481831	2.508072
C	2.797223	-1.045910	1.666868
C	2.277182	-2.698171	-1.811351
H	1.204620	-2.497203	-1.790147
C	2.466339	-4.226958	-1.719227
H	2.045100	-4.637587	-0.799094
H	1.973033	-4.716661	-2.563130
H	3.527681	-4.489387	-1.748334
C	2.810058	-2.178738	-3.158399
H	2.742241	-1.091718	-3.227457
H	3.851538	-2.467350	-3.320449
H	2.222453	-2.606922	-3.974420
C	2.030748	-0.699734	2.939509
H	0.961589	-0.779346	2.735845
C	2.347861	-1.717034	4.054319
H	1.751356	-1.497542	4.943809
H	2.124176	-2.738730	3.738273
H	3.403373	-1.674016	4.336129
C	2.297830	0.738743	3.418105
H	2.078302	1.472560	2.638895
H	1.668686	0.964973	4.282643
H	3.338637	0.874871	3.722259
C	0.870957	2.496124	-1.829752
C	-0.333446	3.385934	-1.495629
C	-0.023308	4.142291	-0.410861
C	1.357799	3.858271	0.018321
C	1.900484	2.920647	-0.797659
C	1.374728	2.692666	-3.274649
H	1.688001	3.730234	-3.417526
H	2.228060	2.044627	-3.487882
H	0.598044	2.466015	-4.006292
C	-1.593889	3.397203	-2.310370
H	-2.279691	4.172664	-1.967213
H	-1.381992	3.590345	-3.367526
H	-2.135197	2.445298	-2.269965
C	-0.885926	5.159967	0.276234
H	-1.868038	5.249272	-0.188178
H	-1.037676	4.898749	1.329127
H	-0.416434	6.149231	0.263030
C	2.001982	4.561327	1.177591
H	3.027951	4.229639	1.338592
H	2.022309	5.644932	1.020026
H	1.445745	4.389333	2.105304
C	3.289501	2.356524	-0.775170
H	3.882173	2.781450	0.035822
H	3.296408	1.268689	-0.648910
H	3.817661	2.564571	-1.712736

Table S8. Cartesian coordinate of **[D]$^{2+}$**

SCF energy (B3LYP/6-311g**) = -1339.18590101 hartree
Solvation: nitromethane with PCM

Atom	Coordinates (Angstroms) X	Y	Z
B	1.545685	-0.105346	2.537126
N	3.579780	0.439477	3.074764
N	1.815425	0.784350	4.991758
C	2.307279	0.376037	3.559553
C	2.335651	-0.336548	1.433847
H	1.923794	-0.718828	0.516155
C	3.604796	0.004020	1.769042
H	4.518034	-0.020230	1.200658
C	0.117025	-0.378800	2.508894
C	-0.315944	-1.688545	2.764981
C	-1.685087	-1.941387	2.665421
H	-2.043600	-2.943702	2.873953
C	-2.598678	-0.948874	2.303578
C	-2.111976	0.327933	2.011045
H	-2.803255	1.103401	1.699347
C	-0.751956	0.636695	2.080974
C	0.640064	-2.812892	3.079137
H	0.108216	-3.649837	3.531305
H	1.441979	-2.514044	3.755643
H	1.113146	-3.180583	2.163013
C	-4.068898	-1.260532	2.184151
H	-4.371251	-2.029758	2.897057
H	-4.299500	-1.634112	1.181099
H	-4.679504	-0.371705	2.351522
C	-0.259544	1.988068	1.624086
H	-1.088680	2.691625	1.551846
H	0.196708	1.912765	0.631985
H	0.490027	2.418155	2.288282
C	4.795663	0.873037	3.746648
C	5.619276	-0.102943	4.332187
C	6.808512	0.331283	4.917634
H	7.453016	-0.404134	5.386821
C	7.193898	1.674559	4.909839
C	6.366959	2.598369	4.267801
H	6.667572	3.639435	4.221565

C	5.170038	2.221642	3.652477
C	5.293955	-1.576127	4.291994
H	5.938298	-2.124908	4.978531
H	5.460333	-1.981248	3.289092
H	4.258246	-1.793279	4.556104
C	8.495957	2.103902	5.536793
H	8.496933	3.171135	5.763045
H	9.330692	1.907952	4.855997
H	8.692748	1.553046	6.458873
C	4.390896	3.232653	2.846790
H	4.662316	4.246579	3.140670
H	3.310941	3.129060	2.947349
H	4.624021	3.125578	1.782575
C	1.639028	-0.032111	6.555513
C	2.566730	1.064534	6.571337
C	1.905219	2.216976	6.023039
C	0.567048	1.833952	5.672627
C	0.401812	0.444718	6.003152
C	1.924436	-1.430868	7.004433
H	1.748557	-1.485902	8.082205
H	2.958740	-1.717115	6.820011
H	1.270916	-2.155169	6.521913
C	3.960553	1.032942	7.109661
H	3.912569	1.365218	8.151067
H	4.628276	1.703373	6.573268
H	4.382510	0.031014	7.099289
C	2.507982	3.574695	5.853927
H	2.337764	4.133384	6.778752
H	2.047146	4.131382	5.040227
H	3.582276	3.525354	5.687843
C	-0.479147	2.719943	5.076994
H	-1.036890	3.176842	5.899361
H	-1.184190	2.160422	4.465547
H	-0.050421	3.522636	4.480206
C	-0.855045	-0.348162	5.841185
H	-1.436292	-0.227161	6.760181
H	-0.658169	-1.409152	5.707376
H	-1.462009	0.004449	5.010544

Table S9. Cartesian coordinate of **[D+Cl]**$^{+}$

SCF energy (B3LYP/6-311g**) = -1799.60924062 hartree
Solvation: nitromethane with PCM

Atom	Coordinates (Angstroms)		
	X	Y	Z
B	12.640114	7.917947	9.597717
Cl	12.688219	9.817457	10.638787
N	10.562054	9.456346	9.038329
N	12.003389	9.123050	9.685113
C	13.702203	7.868667	10.479723
C	14.332956	7.000865	10.556244
H	13.730937	9.050923	11.131983
C	14.386409	9.420475	11.900122
H	12.494614	11.167342	11.143629
C	11.519565	11.418695	12.119082
C	11.448507	12.714567	12.640837
C	10.697536	12.925685	13.395062
H	12.329349	13.723663	12.253427
C	13.320459	13.411963	11.319980
C	14.031080	14.175893	11.022327
H	13.428802	12.143069	10.752776
C	10.585954	10.361109	12.652496
C	11.016177	9.360904	12.596986
H	9.646347	10.342935	12.096065
H	10.346870	10.570940	13.696209
H	12.214798	15.116047	12.822007
C	11.617819	15.753791	12.161538
H	13.195908	15.583922	12.927056
H	11.728255	15.108230	13.799106
H	14.543674	11.852512	9.777439
C	14.948798	12.782754	9.378478
H	14.209816	11.239178	8.940152
H	15.366166	11.318035	10.262607
H	12.346387	6.802168	8.713670
C	13.032082	6.741844	7.487090
C	12.760662	5.667271	6.642701
C	13.275681	5.611457	5.689379
H	11.866413	4.652797	7.001815
C	11.283847	4.705893	8.265847
C	10.635511	3.897248	8.587567
H	11.526259	5.757306	9.157919
C	14.106690	7.737273	7.126027
C	14.384455	7.638317	6.076993
H	15.005955	7.559342	7.724349
H	13.804175	8.769064	7.305196
H	11.556703	3.526253	6.047891
C	12.441570	3.232988	5.478474
H	10.792132	3.832345	5.326107
H	11.178997	2.649246	6.576471

H	10.983711	5.656392	10.562808
C	11.114208	6.569111	11.138119
H	11.499645	4.847670	11.090113
H	9.919629	5.413649	10.552471
H	9.965949	10.793047	8.291752
C	11.017012	11.759296	7.957720
C	11.807415	11.271418	6.922093
C	11.285903	10.012758	6.529701
C	10.157068	9.658157	7.332044
C	8.590663	11.318497	8.679875
C	8.186405	11.938699	7.874500
H	8.644841	11.927435	9.584790
H	7.888688	10.509031	8.868368
H	11.098338	13.106604	8.588856
C	12.080738	13.564373	8.486786
H	10.827776	13.080439	9.644172
H	10.373452	13.764525	8.091362
H	12.975520	11.954048	6.267575
C	13.241201	12.877753	6.780967
H	12.742823	12.210775	5.229531
H	13.863585	11.316132	6.248412
H	11.735396	9.241543	5.336686
C	11.623520	8.166156	5.474605
H	12.762887	9.467750	5.054580
H	11.095651	9.520881	4.488831
H	9.061638	8.772599	6.771732
C	9.450886	7.796027	6.475313
H	8.620172	9.241476	5.886319
H	8.264766	8.604077	7.492297
H	9.301996	8.466562	9.959019

Table S10. Cartesian coordinate of **$AlCl_3$**

SCF energy (B3LYP/6-311g**) = -1623.34446781 hartree
Solvation: nitromethane with PCM

Atom	Coordinates (Angstroms)		
	X	Y	Z
Al	0.000000	0.000000	0.000000
Cl	-0.000158	0.000278	0.000000
Cl	0.000305	0.000000	0.000000
Cl	-0.000158	-0.000278	0.000000

Table S11. Cartesian coordinate of **[$AlCl_4$]$^-$**

SCF energy (B3LYP/6-311g**) = -2083.82709136 hartree
Solvation: nitromethane with PCM

Atom	Coordinates (Angstroms)		
	X	Y	Z
Al	-2.621078	-1.048390	0.000266
Cl	-3.642870	0.722115	0.722495
Cl	-0.576916	-1.048380	0.722713
Cl	-3.642879	-2.818891	0.722491
Cl	-2.621096	-1.048389	-2.167966